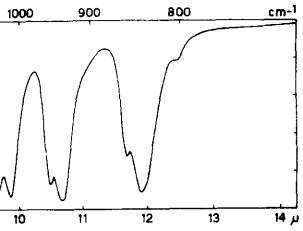
Vorming en reacties van 1,1-diazido-aethers

Sinnema, Yde Abe



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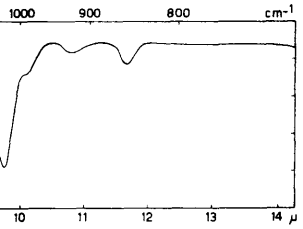

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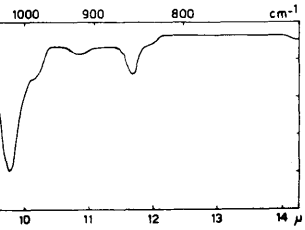

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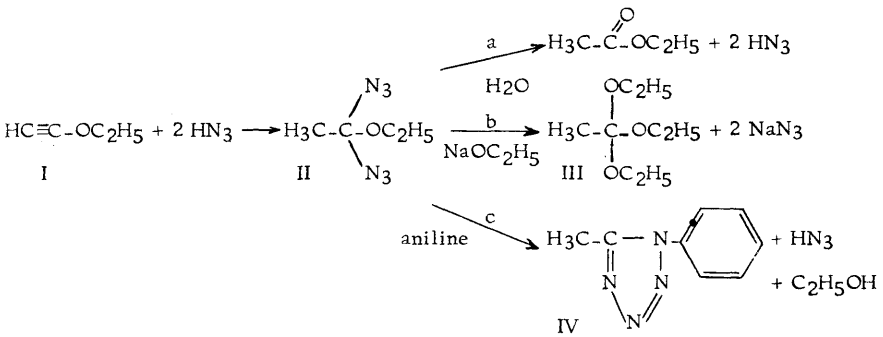
SUMMARY

Chapter I.

In this chapter the reaction of hydrazoic acid with ethoxyacetylene (I) is described. The product of the exothermic reaction is 1,1-diazido-1-ethoxyethane (II) the structure of which has been shown in the following ways:

a) Hydrolysis yields ethylacetate
b) Reaction with sodium ethylate furnishes ethylorthoacetate (III).
c) By reaction with aniline, 1-phenyl-5-methyltetrazole (IV) is obtained.

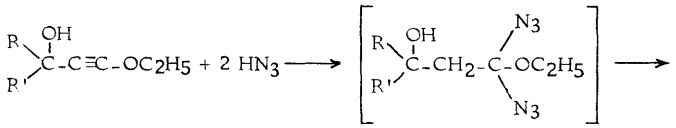


In the same way hydrazoic acid and ethoxypropyne, $H_3C-C\equiv C-OC_2H_5$, yield 1,1-diazido-1-ethoxypropane. It is not possible to add only one mole of hydrazoic acid to these acetylenic ethers.

The reaction between hydrazoic acid and ethylthioacetylene requires prolonged heating and yields 1,2-bis ethylthioethylene. This peculiar result has not been fully explained.

Chapter II.

The reaction of hydrazoic acid with ethoxyethynyl carbinols is described. Very probably the proximate product is also a diazide, but an azido group is replaced afterwards by hydrogen, possibly by the following reactions:



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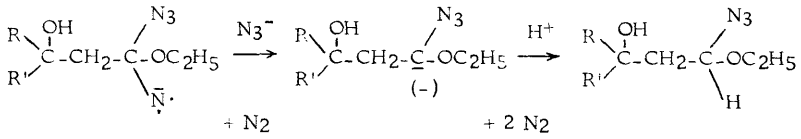
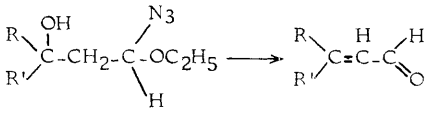


The structure of the finalproduct is confirmed since an α,β unsaturated aldehyde is formed by acid hydrolysis.



The overall result is a modification of the synthesis of α,β unsaturated aldehydes from ethoxyethynyl carbinols, which is usually carried out by partial catalytic reduction of the triple bond and rearrangement of the ethoxyvinyl carbinol formed. The new modification may be useful in cases, where catalytic reduction is impossible.

The third and following chapters of this thesis deal with nucleophilic substitutions in 1,1-diazido-1-ethoxyethane.

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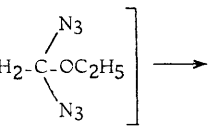

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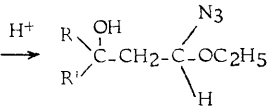

N2

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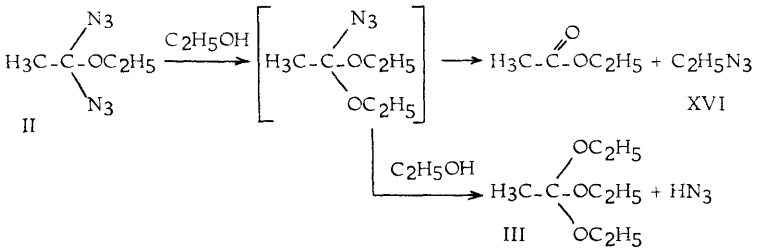
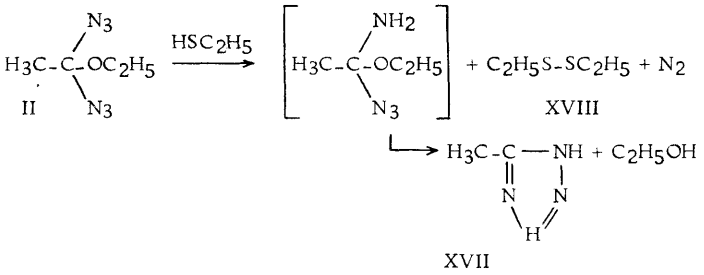
Chapter III.

The reaction of 1,1-diazido-1-ethoxyethane (II) with ethanol yields ethylacetate, ethylazide (XVI) and some ethylorthoacetate (III).

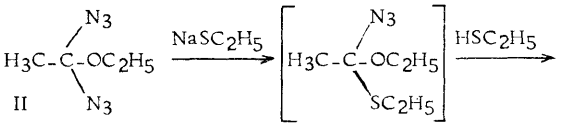


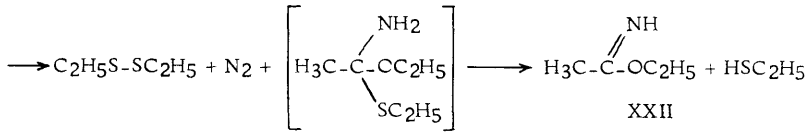
The latter compound can be obtained in considerably better yield by using sodium ethanolate in ethanol.

The reaction with ethanethiol proceeds in a different manner from that with ethanol. Nitrogen is evolved and 5-methyltetrazole (XVII) and diethyldisulfide (XVIII) are obtained in small yields.

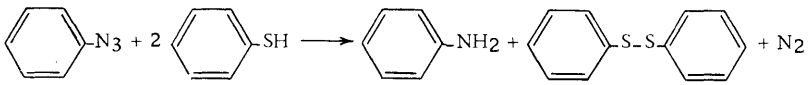


The reaction of sodium ethanethiolate in ethanethiol furnishes acetiminoether (XXII) and diethyldisulfide in good yields.



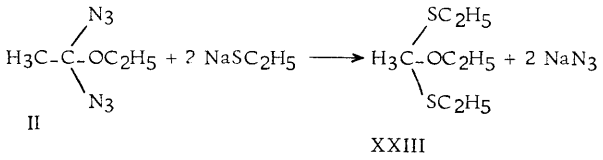


In both cases ethanethiol obviously reduces an azido-group. A similar reduction is observed in the reaction of phenylazide with thiophenol. Here aniline, diphenyl-disulfide and nitrogen are formed.



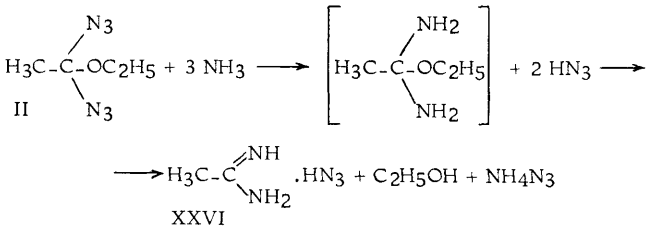
The reduction of azide groups by thiols is a new and possible general reaction.

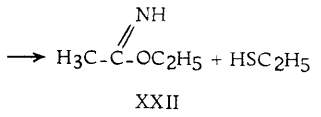
The reaction of 1,1-diazido-1-ethoxyethane with sodium ethanethiolate in a solution of ethanol yields 1,1-bis ethylthio-1-ethoxyethane (XXIII).



Chapter IV.

Ammonolysis or catalytic reduction of 1,1-diazido-1-ethoxyethane (II) yields the same compound, viz. acet-amidiniumazide (XXVI). In the second case probably ammonia is first formed by reduction of azido groups.





XXII

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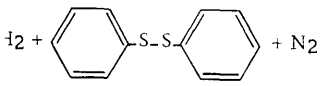

by thiols is a new and

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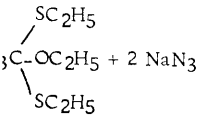

XIII

ction of 1,1-diazido-1-
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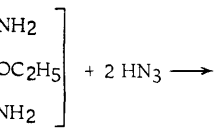
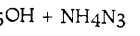


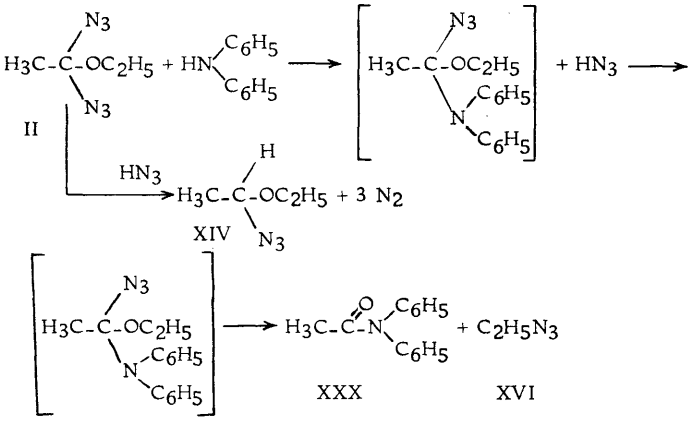


The reaction of II with primary and secondary amines proceeds in a variety of ways. With n-butylamine an exothermic reaction takes place, and N,N'-di-n-butylacetamidiniumazide is obtained in a good yield.

The reaction with diethylamine furnishes mainly tars and some diethylammoniumazide

The reaction with aniline which yields 1-phenyl-5-methyltetrazole (IV) has been mentioned already in the summary of chapter I.

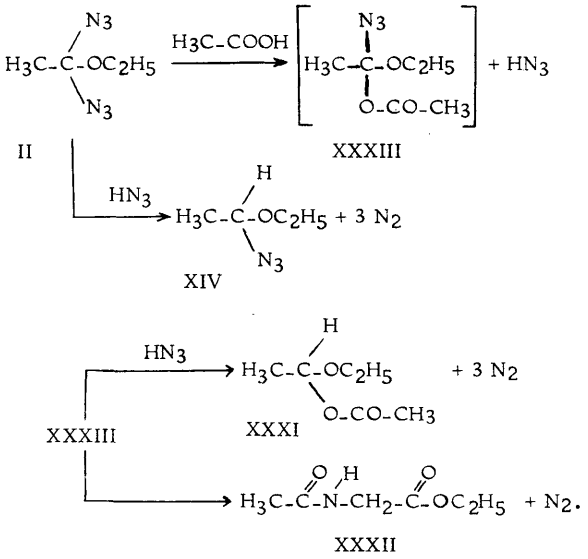
By reaction with diphenylamine, acetyl-diphenylamine (XXX), ethylazide (XVI) and 1-azido-1-ethoxyethane (XIV) are obtained.



XIV XXX XVI

Chapter V.

The reaction of 1,1-diazido-1-ethoxyethane (II) with acetic acid yields 1-azido-1-ethoxyethane (XIV), 1-ethoxy-1-acetoxyethane (XXXI) and nitrogen.



During this reaction also ethyl-N-acetylglycinate (XXXII) is formed.

We presume that 1-azido-1-ethoxy-1-acetoxyethane (XXXIII) is also an intermediate in the reaction leading to this substance, but this needs further examination.